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R. Twells

The Use of Zinc Sulphide as an
Opacifier

**THE USE OF ZINC SULPHIDE AS AN
OPACIFIER WITH SOME NOTES ON
THE RESULTS OF ATTEMPTS TO
PRODUCE LUMINOUS ENAMELS**

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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P A R T I

I INTRODUCTION

According to Staley¹ opacifying agents in enamels are divided, according to their effectiveness, into true opacifiers and accessory opacifiers. The true opacifiers are those capable of making an enamel completely opaque. This class includes compounds of tin, antimony, zirconium, titanium, arsenic, and calcined spinels. The accessory opacifiers are those which are minor aids in producing opacity. This class includes bone ash, silica, and the various compounds of fluorine. Staley further states that the true opacifiers are not themselves opaque. Their opaqueness is due to their insolubility, fine state of subdivision, and last and most important to their high indices of refraction.

The opacifying agent most employed in commercial enameling is SnO_2 . It is by reason of its cost and the quantity employed the most expensive constituent used in ordinary enameling. None of the other true opacifiers is able to completely equal SnO_2 in effectiveness. Antimony is poisonous, and produces a yellow-tinged enamel unless the composition is correct. Zirconium is too expensive. Titanium gives a yellowish enamel that tends to chip. The use of the spinels is still in the experimental stage. Arsenic oxide is a deadly poison. Some use has been made of ZnS as an opacifier in Germany, but little is known as to its value in America.

The purpose of this thesis is to determine what conditions lead to the development of opacity with ZnS , and to discover if it looks promising for commercial use.

1. Technologic paper of the Bureau of Standards No. 142, Materials and Methods used in the Manufacture of Enamelled Cast-Iron Ware, by Homer F. Staley, Metallurgical Ceramist.

II LITERATURE

"Enamels and Glazes" E. de Haen, Chem. Fabrik List. G. m. b. H. Ger., 289, 317, Jan. 14, 1913; Chem. Abstracts, Vol. 10, Part 3, p 2792 (1916). ZnS may be used as a substitute for the heretofore employed ZnO, as a clouding agent for enamels and glazes. Small amounts of ZnS are sufficient to impart complete opacity to the enamel. Even when the melt is transparent, five per cent of the ZnS is sufficient. The sulphide is mixed as a powder with the powdered glaze material. Colors or oxides may be mixed with the mass.

"The Use of ZnS in the Production of White and Luminous Enamels" Dr. J. Schaefer, Keram. Rundschau (25) 75, 1917. In sheet iron enamels of suitable composition ZnS is a good opacifier in the absence of some metallic oxides. The opacity is equal to that from SnO₂, but is not as white nor as brilliant. It can not be used with colored enamels or with the oxides of arsenic, lead, antimony, or manganese. The writer is of the opinion that the opacity cannot be attributed to the conversion of the sulphide to the oxide.

III METHOD OF ATTACK

The work was laid out to determine the practicability of using ZnS as a true opacifier, as this was considered to be of more importance than its use as an accessory opacifier. It was decided to use sheet steel trial pieces for the experiments as they are easier to obtain and handle than cast iron. A good ground coat was next chosen. Since the time to be devoted to this experiment was limited, it was not intended to vary the range of composition of the ground coat, but to pick such a one as would make a uniformly good coat. A good cover coat was also chosen. With it as a basis a short investigation was carried out to determine the best manner in which ZnS

could be introduced into the cover coat, and the proper manner in which to carry on the burning process. After the preliminary investigation it was decided that several fields of investigation should be laid out in order to determine whether varying the amounts of certain constituents would affect the opacity.

IV TRIAL PIECES

The trial pieces used were stock sheet steel 2 1/4" x 3". The steel in these trial pieces did not prove altogether satisfactory as they proved difficult to pickle, and undoubtedly had some tendency to cause blistering. A few pieces of a higher grade of steel were used. These pickled easily, and showed no tendency to cause blistering.

The trial pieces were scaled in a muffle kiln at a temperature of 750°C. to 850°C. The purpose of this process is to burn off the grease. Should the temperature be less than 750°C. all of the grease will not be removed. If the temperature goes too high the metal will lose its ductility. Close packing of the pieces is to be avoided as it leads to unequal heating conditions. The pieces were kept in the furnace until they showed a uniform black or velvet color.

The pickling was done by placing the trial pieces in a porcelain dish with a solution of one part of concentrated HCl and six parts of water. A small amount of the old pickling fluid was added. The solution was warmed gently, and the pieces were stirred occasionally. After 35 to 45 minutes of this treatment, the trial pieces were dumped into warm water. They were now sponged to remove any black scale that still remained attached, and, after being

rinsed in another pan of hot water, the pieces were placed in a hot solution of Na_2CO_3 of such strength as to feel soapy to the touch. The trial pieces were carried near the dryer in the Na_2CO_3 solution before removing. By means of a sponge the excess of solution was wiped off, and the pieces were set in the dryer on edge in such a way as to touch the support in the least possible manner. When the above process was carefully carried out, the pieces were well pickled. Their cleaned surface was now a bright grey. If the above method was not followed, black or rusty pieces invariably resulted.

V COMPOSITION OF GROUND COAT

The ground coat used was taken from the work of Shaw.² Mr. Shaw took the formulas of five commercial ground coats, and took the average of the average of the ingredients contained on them. The result gave him the following enamel.

Empirical Formula		Batch Weight in Equivalents	
0.15	K_2O	0.10	Feldspar
0.60	Na_2O	0.77	Flint
0.24	CaO	0.19	Borax
0.006	CoO	0.22	Soda
0.004	MnO_2	0.06	KNO_3
		0.24	Flucrspar
		0.06	Cryolite
		0.006	Cobalt
		0.004	MnO_2

Mill Addition

5% Raw Clay

2% Hot Borax

Using this formula as a basis, he varied the amount of SiO_2 between 1.5 to 1.7 equivalents, the amount of B_2O_3 between 0.0 to 0.7 equivalents, and the amount of Al_2O_3 between 0.1 to 0.5

2. Allowable Limit of Variation in Ingredients of Enamels for Sheet Steel., T.A.C.S., Vol.11.

equivalents. He next varied the Na₂O at the expense of the CO₃O₄, the Na₂O at the expense of the CaO, the K₂O at the expense of the Na₂O, the feldspar at the expense of the cryolite, and finally he varied the whiting and fluorspar. As a result of this work he gave the following range for ground coats.

Range for Ground Coats

K ₂ O	0.15 - 0.75	}			
Na ₂ O	0.00 - 0.6				
CaO	0.14 - 0.64		Al ₂ O ₃	.1 - 0.5	} SiO ₂ 1.1 - 1.7
CoO	0.00 - 0.6		B ₂ O ₃	.2 - 0.5	
MnO ₂	-----				

By examining his results, the number of equivalents of each ingredient that gave the best results was determined, and the following enamel was picked for use.

Ground Coat Used

Empirical Formula

0.15	K ₂ O	}			
0.60	Na ₂ O				
0.24	CaO		0.3	Al ₂ O ₃	} 1.5 SiO ₂
0.006	CoO		0.4	B ₂ O ₃	
0.004	MnO ₂				

Shaw recommended the use of the actual analysis of the different constituents as far as possible. It was thought that the feldspar was most likely to vary from its theoretical composition; so its analysis alone was used.

Analysis		Empirical Formula	
SiO ₂	70.9	CaO	0.102
MgO	tr.	FeO	0.019
CaO	0.9	KNaO	0.854
Al ₂ O ₃	16.5	RO	0.975
Fe ₂ O ₃	0.2		
KNaO	11.5		
Ig.	---		

Al₂O₃ (7.63 SiO₂

Mol.Wt. 640

The batch weight of the ground coat was then determined in the usual way to be as follows:

Batch Weight		Mill Addition	
Feldspar	73.5	Ivory Fat Clay	12.9
K ₂ CO ₃	6.9	Borax	3.0
Borax	73.5		
Cryolite	56.7		
Flint	30.0		
Whiting	18.0		
Fluorspar	3.9		
Co ₃ O ₄	0.5		
MnO ₂	0.35		

VI PREPARATION AND APPLICATION OF GROUND COAT

The ground coat was weighed out, mixed thoroughly by putting it several times through a 20 mesh sieve, and finally fritted in a drop frit furnace. After fritting the water was poured off the frit, and it was allowed to dry. It was then again fritted in the same manner to insure that the frit was free from all gases, or in other words, to insure that all reactions were complete at a temperature higher than that which would be employed in putting it on the

steel. The frit and mill charge were wet-ground in a ball mill to pass 150 mesh.

Before applying the ground coat the trial pieces were sponged on the enamel side in order to insure that all dust was removed. The pieces were next dipped in the coat, and placed in a steam-heated dryer. Care was taken that the ground coat was of such consistency when used that it would form a smooth coating over the piece and yet would not collect along the edges.

VII BURNING

The burning was done in a muffle gas fired kiln. The kiln proved very easy to regulate, and little trouble was experienced in maintaining the exact temperature wanted, as well as the kiln atmosphere needed. The temperature of burning was varied from 850°C. to 950°C. It was found that the higher the temperature used, the less time was needed in which to heat the enamel. The higher temperatures, however, proved unsuitable since it was too difficult to withdraw the trial at the proper time. According to Shaw³, the disappearance of the blue color is considered to be a mark of good burning; hence as far as possible the pieces were withdrawn at this stage. Seventy-five seconds in the furnace at a temperature of 900°C. was found to be best, and this was used in applying all the ground coat on all trial pieces. The result of the application and burning was a smooth lustrous ground coat.

VIII SELECTION OF COVER COAT

The cover coat was also chosen from the work of Shaw. Shaw took the formulas of five commercial cover coats, and made an

3. Ibid.

average of the ingredients used. This gave an enamel of the following composition:

Cover Coat Used

Empirical Formula			Batch Weight	
0.15	K_2O	} 0.2 Al_2O_3 { 1.6 SiO_2	Feldspar	73
0.50	Na_2O		Borax	36
0.35	CaO		Fluorspar	11
			Whiting	8
	Mill Addition		Soda Ash	20
	5% Raw Clay		Eng. C. Clay	11
	3% Borax		Flint	24

Since Shaw reported this to be a good cover coat, it was adopted as the basis for the experimental work in varying the composition of the cover coat.

IX PREPARATION AND APPLICATION OF THE COVER COATS

The fritting was done as with the ground coat, care being taken that the reactions were complete at a higher temperature than would be used in the enameling oven. The mill charge was wet ground in a ball mill to 150 mesh. The coats were set at such consistency as to form a smooth layer on the ground coat without collecting at the edges. The trial pieces were fired in the muffle kiln as before, a temperature of $875^{\circ}C$ for two minutes being used.

X PRELIMINARY EXPERIMENTS

Before proceeding further it was thought well to determine what method of adding the ZnS , and what kiln atmosphere would give the best results. With this in mind the following methods of fritting and firing were tried to determine what methods should be used in the main experiments.

1. Two cover coats each containing ten per cent of ZnS as part of the mill charge were burned, one in an oxidizing atmosphere, and one in a strongly reducing atmosphere.

Result: It was found possible to burn out all traces of the ZnS in a strongly oxidizing atmosphere leaving a transparent glassy coating upon the ground coat. There seemed little tendency to bubble and blister. Where a strongly reducing atmosphere was used, an opaque white cover coat was obtained, but there seemed to be a greater tendency to blister.

2. Ten per cent of the batch weight of ZnS was fritted with the batch. The fritting was done as described above. Precautions were taken to keep the crucible covered, and to use a strongly reducing atmosphere in the frit furnace.

3. Ten per cent of the batch weight of ZnS was added in the mill charge, and it was burned under reducing conditions.

4. Fifteen per cent of the batch weight of ZnS was added in the mill charge, and it was burned under reducing conditions.

Results of 2, 3, and 4: Practically no difference was discernible between these methods of adding the ZnS. In each case an opaque coating was obtained. The color was darker than would be obtained with a tin enamel. On first putting the trial pieces in the furnace, considerable bubbling occurred, but by leaving the piece in the furnace for some time, the surface became fairly smooth. Whether the bubbling was due to the ZnS in the coat, or whether it was due to improper preparation and burning was not determined.

XI SCOPE OF INVESTIGATION

Since ten per cent of ZnS in the mill charge gave good results, this was taken as the amount to be used in further experimentation.

In burning all the remaining pieces a reducing atmosphere was used. Taking the cover coat used in the preliminary experiments as a basis, the following series were made up to determine what effect the variation in the constituents would have upon the bubbling and opacity.

Series.1.- This series was carried out by varying the B_2O_3 and SiO_2 , keeping the R.O. the same, and the Al_2O_3 constant at 0.15 equivalents. The intermediate numbers were obtained by blending the four corners in accordance with their molecular formulas. The corner members were made up by fritting all but the raw clay and the ZnS. The mill charge of each corner was ground to pass 150 mesh, and the blending was done with the slips.

Batch Weights of the Corners in Equivalents

The ceramic formulae are shown on the diagram

	1	4	13	16
Feldspar	0.1	0.1	0.1	0.1
K_2CO_3	0.05	0.05	0.05	0.05
Fluorspar	0.2	0.2	0.2	0.2
Whiting	0.15	0.15	0.15	0.15
Soda Ash	0.37	0.37	0.3	0.3
SiO_2	0.5	1.1	0.5	1.1
ZnS	10.0	10.0	10.0	10.0
Raw Clay	0.05	0.05	0.05	0.05
Borax	0.125	0.125	0.2	0.2

Results: See diagram.

Series 2.- This series consisted in keeping the Al_2O_3 constant at 0.2 equivalents, and varying the B_2O_3 and SiO_2 .

Batch Weights of the Corners in Equivalents

The ceramic formulae are shown on the diagram

	1	4	13	16
Feldspar	0.15	0.15	0.15	0.15
Fluorspar	0.2	0.2	0.2	0.2
Whiting	0.15	0.15	0.15	0.15
Raw Clay	0.05	0.05	0.05	0.05
Borax	0.125	0.125	0.2	0.2
Soda Ash	0.37	0.37	0.3	0.3
SiO ₂	0.2	0.8	0.2	0.8
ZnO ₂	10.0	10.0	10.0	10.0

The fritting, milling and blending was done as for Series 1.

Results: See diagram.

Series 3.- This series consisted in keeping the Al₂O₃ constant at 0.25 equivalents and varying the B₂O₃ and SiO₂ as follows:

Batch Weights of the Corners in Equivalents

The ceramic formulae are shown on the diagram

	1	4	13	16
Feldspar	0.15	0.15	0.15	0.15
Fluorspar	0.2	0.2	0.2	0.2
Whiting	0.15	0.15	0.15	0.15
Raw Clay	0.05	0.05	0.05	0.05
Borax	0.125	0.125	0.2	0.2
Soda Ash	0.37	0.37	0.3	0.3
SiO ₂	0.1	0.7	0.1	0.7
ZnO ₂	10.0	10.0	10.0	10.0
Calcined Clay	0.05	0.05	0.05	0.05

The fritting, milling, and blending was done as for Series 1.

Results: See diagram.

XII SUMMARY OF RESULTS

Series 1, 2, and 3, are most opaque in the order named. Increasing the Al_2O_3 increases the opacity. This agrees with the results obtained by Brown in studying the use of antimony oxide as an opacifier.⁴ It also agrees with the work of Shaw using SnO_2 as an opacifier.⁵

Increasing the SiO_2 leads to shivering as is to be expected. An increase of SiO_2 leads to decreased opacity, except in the case of low Al_2O_3 where it seems to increase the opacity slightly.

Increasing the B_2O_3 leads to increased opacity, but it also leads to bubbling and shivering. The best results were obtained with Series 2. From the preliminary and general experiments, No. 11 appeared to be the best part of the field.

XIII GENERAL CONCLUSIONS

The use of ZnS burned in a reducing atmosphere gives an opacifying agent for use in a cover coat. In no case does it seem to give a pure white coat. At best it gives a coat tinged with green or brown. It may be possible to use it as an accessory opacifier, and experiments could be done to determine its suitability for such work. Its use seems to lead to bubbling. Whether this is due to the use of the ZnS , or whether it is due to poor methods of compounding and firing the enamels was not determined. The recommendation of Dr. Schaefer would naturally lead one to expect better results than were obtained with the compositions and firing conditions

4. R.E. Brown, University of Illinois Bulletin No. 18. The Replacement of Tin Oxide by Antimony Oxide in Enamels for Cast Iron.

5. Shaw. Allowable Limit of Variation in Ingredients of Enamels for Sheet Steel. T.A.C.S. Vol. 11.

Series I

0.15 K_2O 0.50 Mn_2O 0.35 CaO .15 Al_2O_3 .25 - .4 B_2O_3

{ 1.2 -

1.8 SiO_2

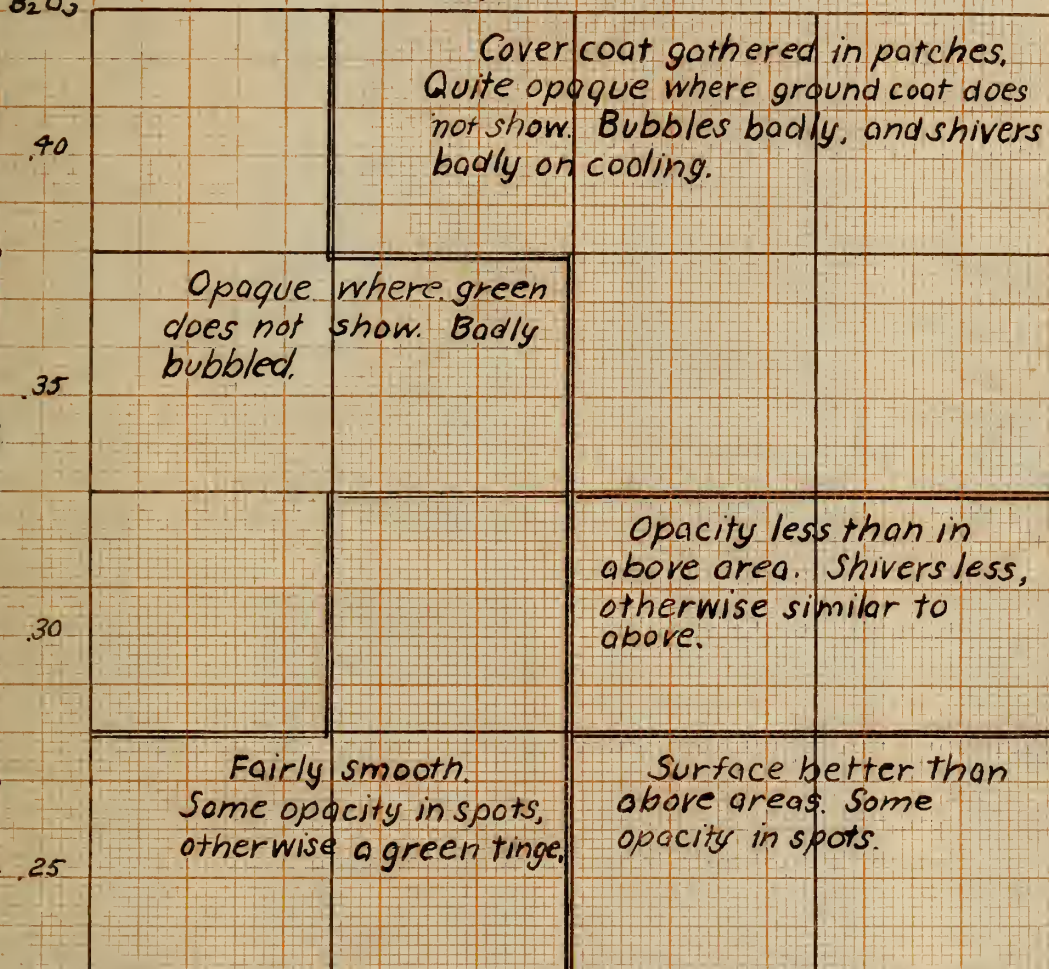
100% ZnS

shivering increases.

Equivs.
 B_2O_3

Bubbling increases.

Opacity increases



shivering increases.

Opacity increases

1.2

1.4

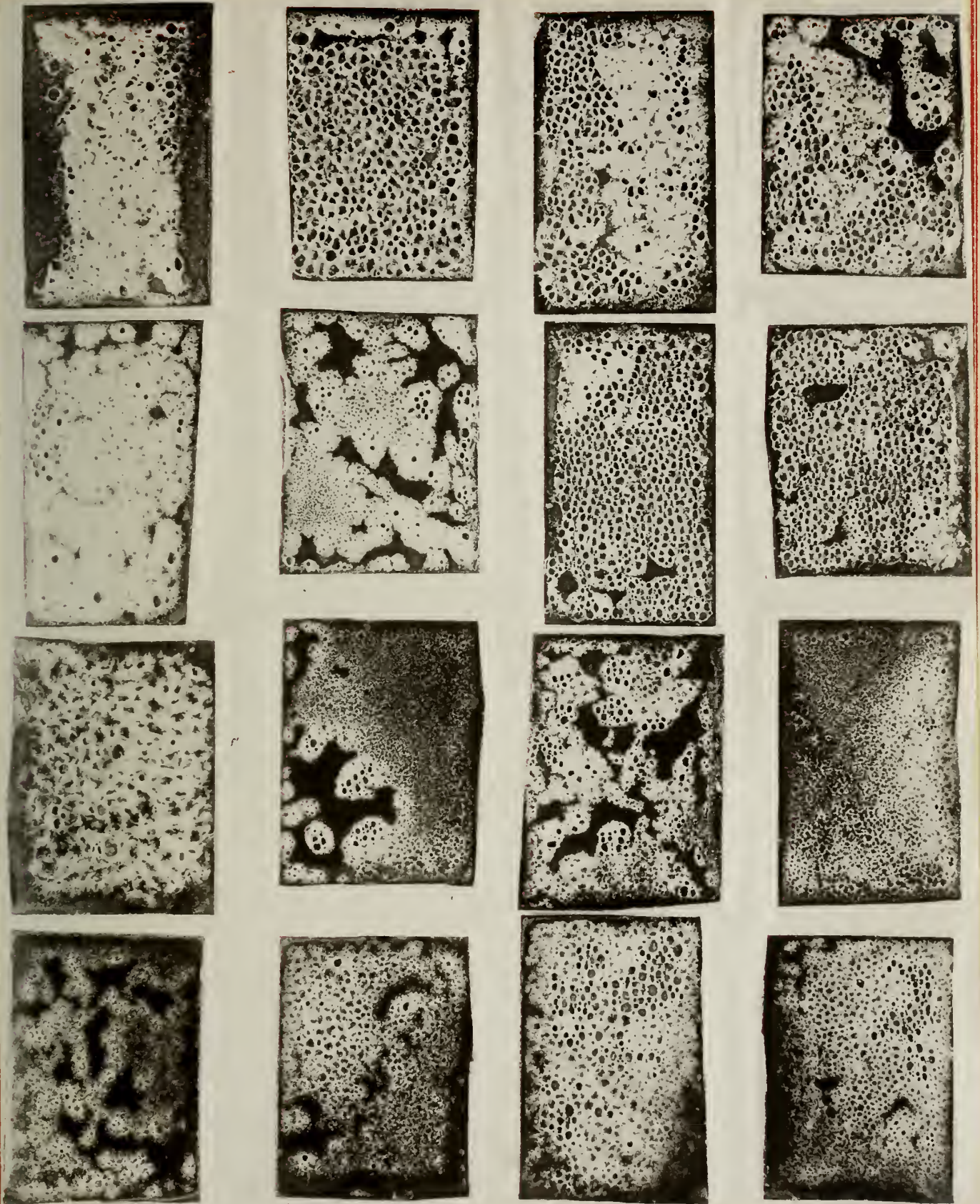
1.6

1.8

Equivs.
 SiO_2

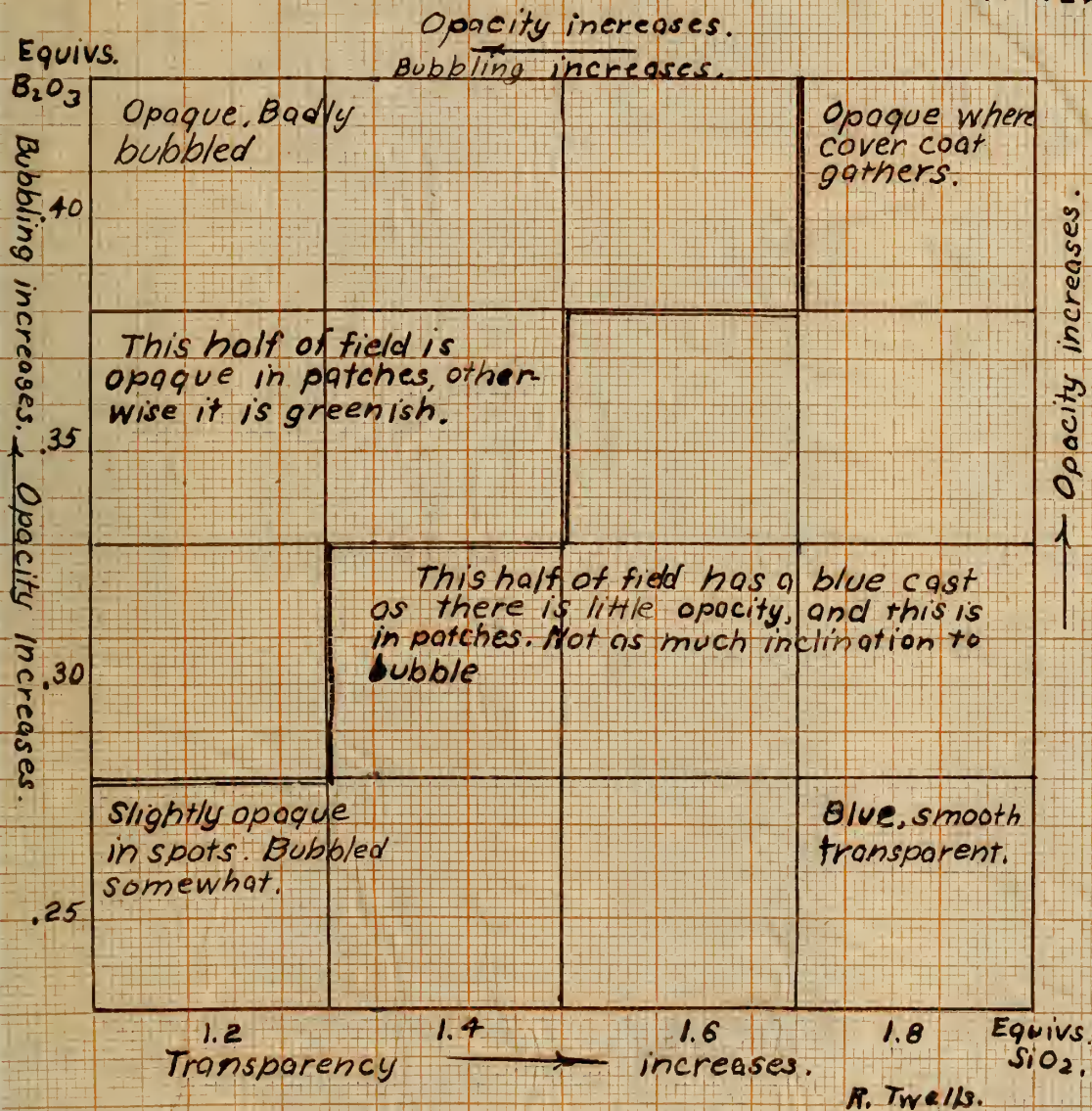
Opacity increases.

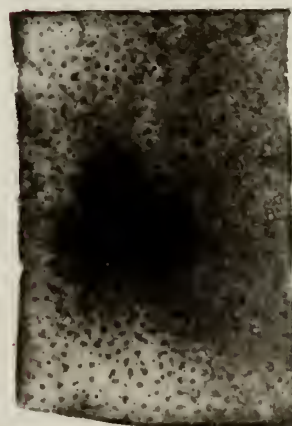
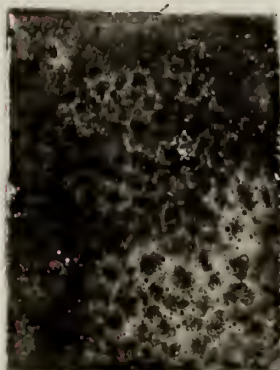
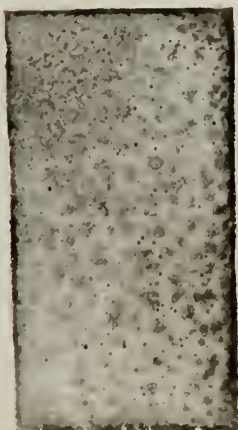
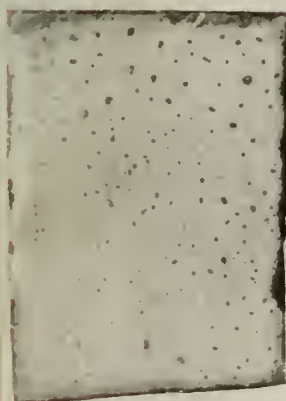
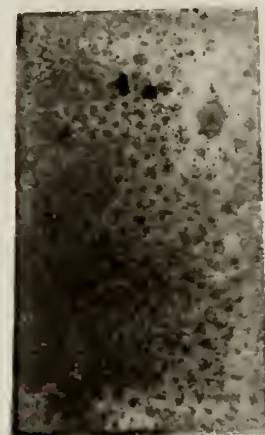
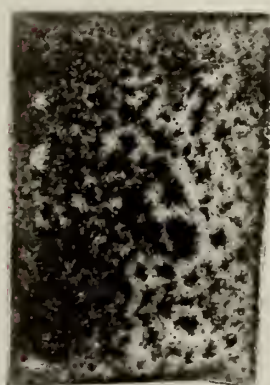
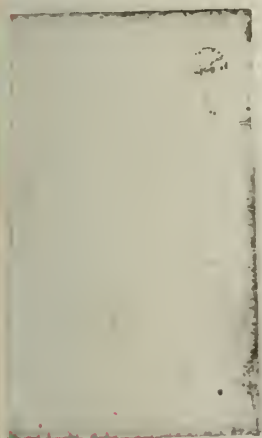
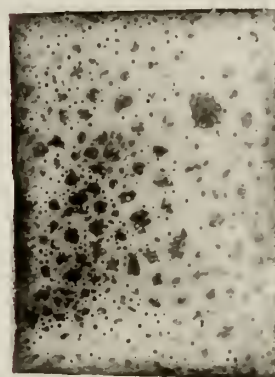
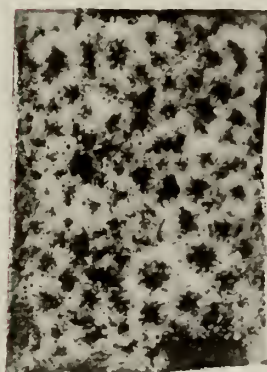
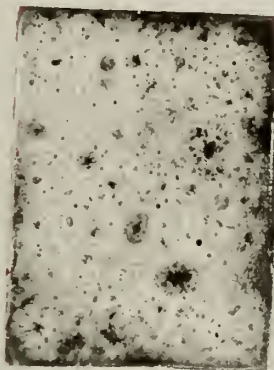
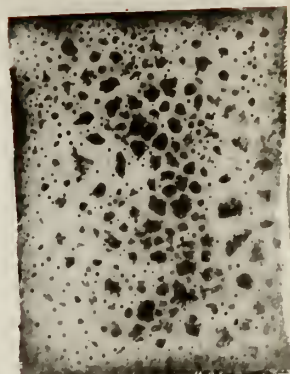
R. Twells.



Series I.

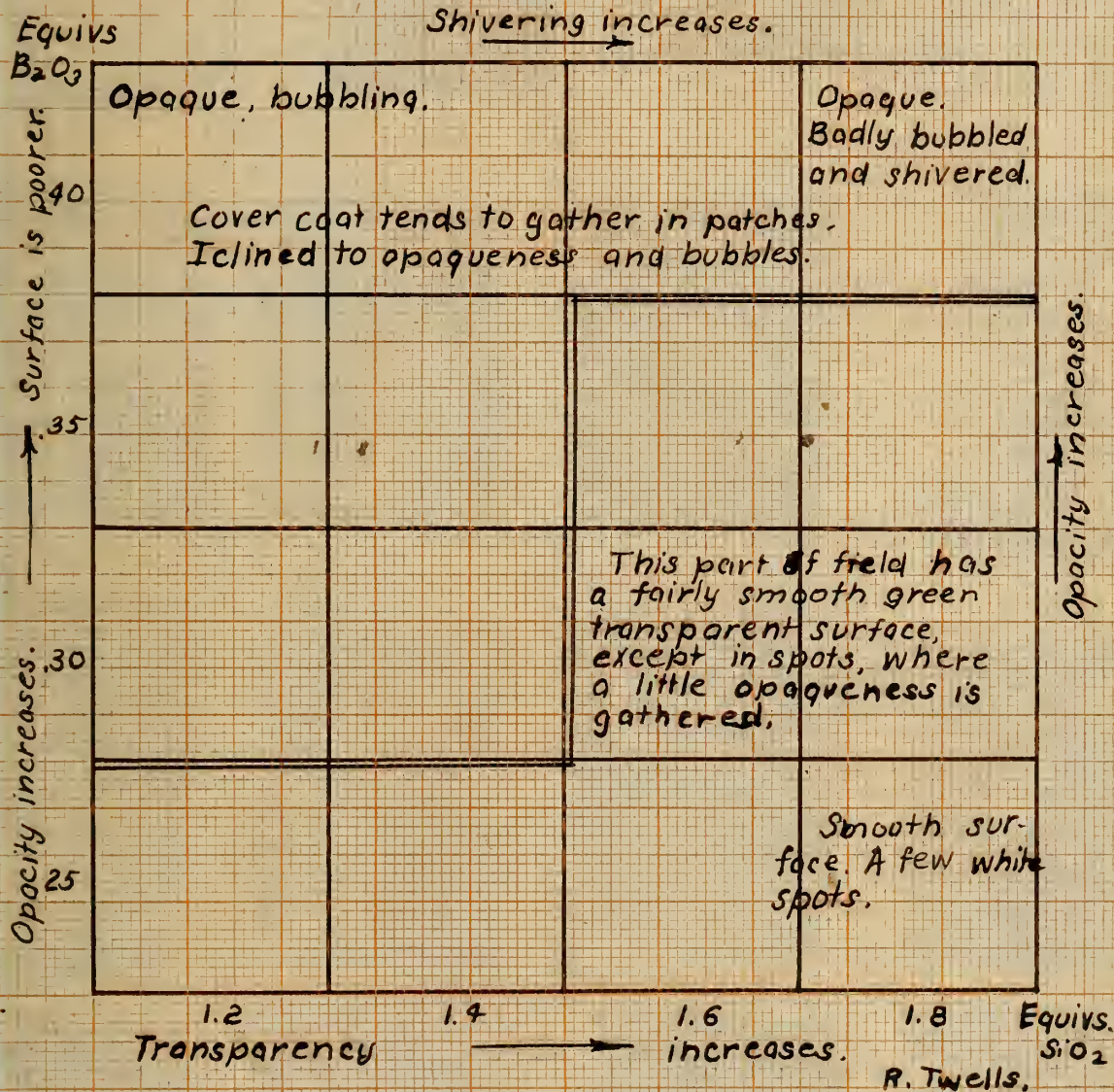
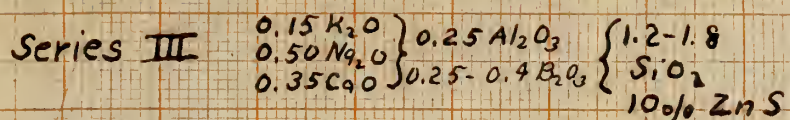
Series II $\left. \begin{array}{l} 0.15 \text{ K}_2\text{O} \\ 0.50 \text{ Na}_2\text{O} \\ 0.35 \text{ CaO} \end{array} \right\} \left. \begin{array}{l} 0.20 \text{ Al}_2\text{O}_3 \\ 0.25 \text{ B}_2\text{O}_3 \end{array} \right\} \left. \begin{array}{l} 1.2- \\ 1.8 \text{ SiO}_2 \\ 10\% \text{ ZnS} \end{array} \right\}$

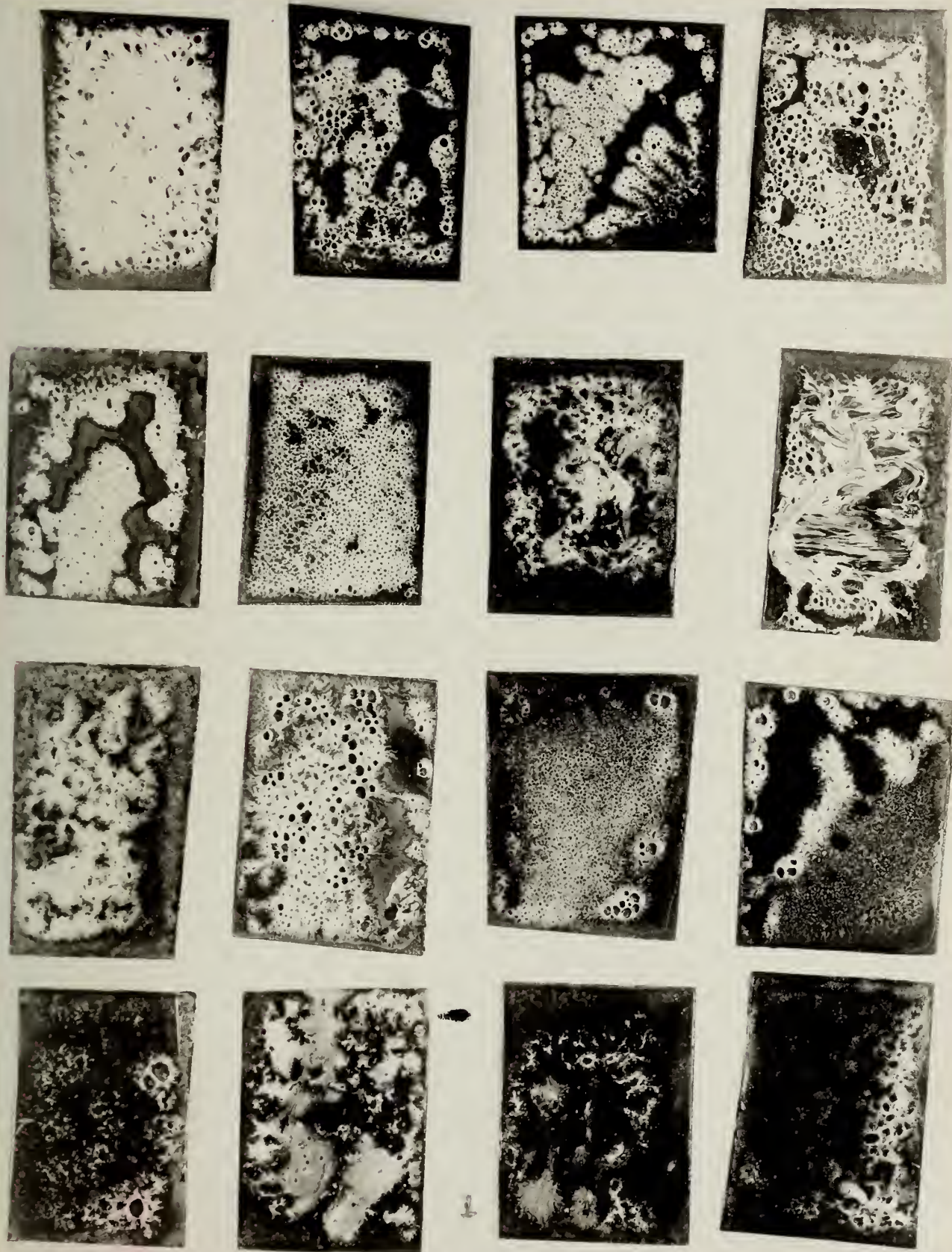




Series II

Series III





Series III.

used.⁶

P A R T I I

I INTRODUCTION

The production of luminous paints and enamels proved to be important during the war. Luminous paints were used on aeroplane dials. Luminous enamels were needed for watch dials. Many other practical uses might be mentioned.

Luminous pigments for paints consist of two kinds:

1. Those pigments whose luminosity is produced by means of ZnS, and a very small amount of a radium salt. The life of such a pigment would be 1700 years. By using meso-thorium instead of radium pigments could be produced that would last for several years. The pigments produced in this way are called self-luminous.

2. Those pigments whose luminosity is developed by exposing them to a strong light. This luminescence is not permanent, but may be renewed. This type consists of the sulphides of calcium, strontium, barium, and zinc, and the thiosulphates of strontium and barium.

The luminous enamels in use are of the self-luminous type. It is evident that this makes the production of luminous enamels very expensive.

The purpose of these notes is to suggest, and possibly pave the way for some work towards using cheaper substances to produce luminosity in enamels.

II LITERATURE

1. F.H. Clew. "Luminous Paints and Enamels" Ind.Chemie, Vol. 88, p 653, 1916. (Not accessible for reference).
6. Keram. Rundschau, 25-73, 1917.

2. "The Use of ZnS in the Production of White and Luminous Enamels" Dr. J. Schaefer, *Keram. Rundschau* (25), p 75, 1917. Phosphorescent ZnS in an enamel will give a luminous enamel that holds its luminosity for several years.

3. Am. Pat. 1, 202, 825. Chas. H. Viol. A first coat of white or transparent glaze is applied to the object to be coated. After firing there is placed on this surface a phosphorescent compound such as ZnS containing a radium salt, such luminous material being mixed with enough of the glaze to become incorporated in it upon firing.

4. Eng. Pat. Gazette, Nov. 1913, p 1163. Luminous ZnS can be added to low temperature enamels, high luminosity being obtained by the addition of 20 percent to 30 per cent. Exposure to daylight or artificial light will render such an enamel luminous for a considerable time.

III METHOD OF ATTACK

Due to the cost and scarcity of radium and meso-thorium salts, it was decided to use ZnS and the sulphides of the alkali earths. By making up several pigments such as had proved successful in luminous paints it was thought that possibly the same effects could be obtained in enamels. These pigments after being made were to be mixed in a standard cover coat in certain per cents, and after firing, the trial pieces were to be exposed to strong light. If by the use of any one of the pigments tried, successful results were obtained, it would then be possible to lay out fields to determine the compositions of pigments or of cover coats that would produce the best results.

IV TRIAL PIECES AND GROUND COAT

The trial pieces used were similar to those used in the work with ZnS as an opacifier. They were carefully scaled and pickled in a manner such as has been described. The ground coat used is the same one that was used in the work with ZnS as an opacifier. It was applied and burned in the same manner.

V PIGMENTS USED

For mixing with the cover coat, the following pigments were prepared. The substitutions made are due to inability to get certain materials.

1. Similar to Leonard's formula given in the Scientific American Encyclopedia of Formulas, Hopkins, p 639, with an equivalent amount of $\text{Ba}(\text{OH})_2$ substituted for strontium carbonate.

$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	214 Pts.
Sulphur	100
KCl	0.5
NaCl	0.5
MnCl_2	0.4

2. Leonard's formula given in the Scientific American Encyclopedia of Formulas, Hopkins, p 639, for luminous paints was used. Its composition is as follows:

Strontium Carbonate	100.0 Pts.
Sulphur	100.0
KCl	0.5
NaCl	0.5
MnCl_2	0.4

3. Vaninc's formula given in the Twentieth Century Book of Formulas for luminous paints was used with an equivalent amount of

barium thiosulphate substituted for strontium thiosulphate.

Barium thiosulphate 75 Pts.

12 parts by weight of a 0.5% acidified alcoholic solution of $\text{Bi}(\text{NO}_3)_3$.

6 parts by weight of a 0.5% acidified alcoholic solution of $\text{Ur}(\text{NO}_3)_3$.

4. Balmain's formula given in the Twentieth Century Book of Formulas for luminous pigments with CaCO_3 substituted for CaO .

Whiting	36 Pts.
Sulphur	6
Starch	2
KCl	0.15
NaCl	0.15

1 part by weight of a 0.5% acidified alcoholic solution of $\text{Bi}(\text{NO}_3)_3$.

5. CaS made up as follows: 2 1/4 parts of CaO and 1 part of flowers of sulphur were boiled together for 1 hour. They were then set aside in a covered vessel for a few days, and at the end of this time the excess water was poured off. The crystals left were carefully dried, and calcined as described below.

6. 12 parts of ZnS uncalcined, and 36 parts of CaS prepared as described.

With the exception of No.6 the pigments were mixed carefully and placed in a closed sagger. The saggars were heated to a temperature of 2372°F , and held at this temperature for one hour. The kiln used was gas-fired, and it was kept slightly reducing in temperature. The result of the calcination was an unfused mass which reduced easily to a powder.

VI COVER COAT

The cover coat used was taken from the work of Shaw⁷, but instead of using the average of five commercial enamels as was done to get the cover coat as a basis for variation in the work with ZnS as an opacifier, an effort was made to improve this coat by taking the number of equivalents of each ingredient that Shaw found to be best. The following cover coat was used.

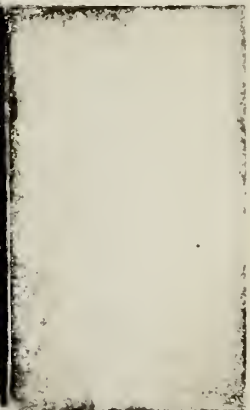
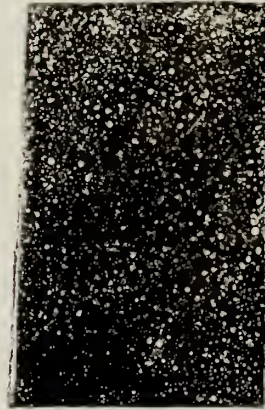
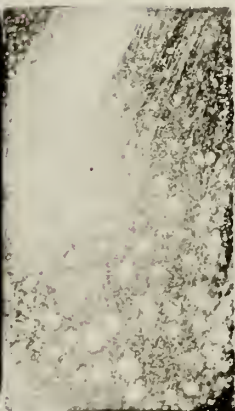
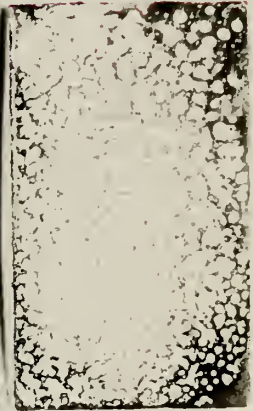
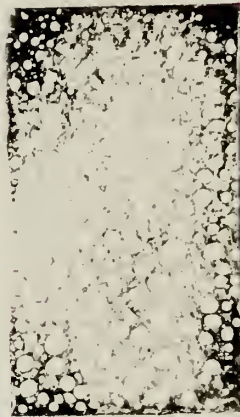
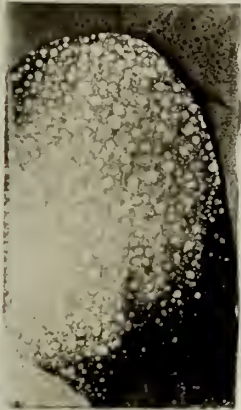
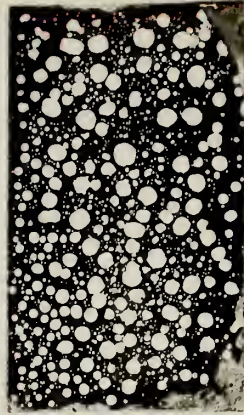
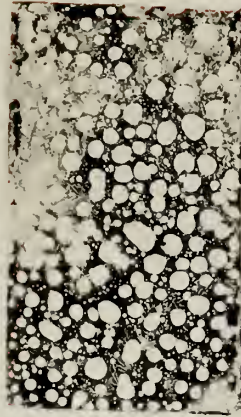
0.15	K ₂ O	}	0.35	B ₂ O ₃	{	1.6	SiO ₂
0.42	Na ₂		0.2	Al ₂ O ₃		0.05	SnO ₂
0.35	CaO						
0.04	ZnO						
0.04	Sb ₂ O ₃						
Batch Weight			Mill Addition				
Feldspar	64 pts.		13 pts.	Ivery fat clay			
K ₂ CO ₃	9		8 pts.	SnO ₂			
Borax	68		10% and 15%	of pigment, called			
Cryolite	21		(a) and (b)	respectively.			
Flucrspar	16						
Whiting	14						
Flint	44						
ZnCO ₃	5						
Sb ₂ O ₃	12						
Soda Ash	9						

The true molecular formula of the feldspar was used as determined from an analysis. The preparation of the cover coat is the same as has been described. The burning was carried on in a muffle, gas-fired kiln with reducing conditions.

7. Shaw. Allowable Limit of Variation in the Ingredients of Enamels for Sheet Steel. T.A.C.S., Vol.11, p 103.

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VII DESCRIPTION OF THE TRIAL PIECES

Since in no case was luminosity obtained on exposing the enamels to light, the only description that can be given is that of the surfaces of the various trial pieces.

1a. A black field covered with small white spots that run together at the center of the trial piece.

1b. Similar to 1a except more spots.

2a. A black field thickly covered with white spots $1/8$ inch to $1/4$ inch in diameter.

2b. Similar to 2a except a few more spots.

Pigment No.2 gave a very peculiar and pleasing effect, and probably would be worth investigating with respect to developing the effect mentioned for decorative purposes.

3a. Large irregular spots running into one another.

3b. Similar to 3a except the piece becomes almost completely white.

4a. Covered with small white spots giving a milky appearance to the piece.

4b. Similar to 4a.

5a. A series of white specks on a dark background.

5b. Similar to 5a.

6a. A dark background covered with specks like salt.

6b. Similar to 6a.

VIII CONCLUSIONS

In regard to the surfaces produced by the use of these pigments in an opaque tin-antimony enamel, it appears that all these substances have a marked tendency to cause a segregation of the white cover coat into spots upon the ground coat. The character of the

spots varies greatly with the kind of pigment used, and but little with its amount. The sulphides of calcium seem to produce small scattered spots; the sulphides of barium do similarly; the sulphides of strontium produce large distinct spots; and the thiosulphate of barium produces large irregular spots. The question naturally arises as to how much of the sulphide actually remained in the enamel as such. If very little remained it would account for the fact that no luminosity was obtained. For the reason that at best the reducing conditions are not very strong in a small muffle kiln where the door is being frequently opened, it is the writer's opinion that very little of the sulphide remained in the enamel after burning. In view of the work of McDougal Stewart and Wright⁸, the question of wet or dry grinding is undoubtedly an important factor. By using more exact methods and less pure materials it probably is possible to produce luminous enamels by the methods suggested and started. Due to the short amount of time available, no further work along these lines has been possible.

8. Phosphorescent ZnS. J.O.C. 1917, Vol.III, p 663.

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U.S. Pat. No.1097379. C.P.Karr. ZnO, BaCO_3 , Hydrogel, BaSO_4 , Asbestine hydrogel, colloidal ZnSO_4 , Barium hydro-sulpho-oxide impregnated with Ra emanations.

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McDougal, Stewart, and Wright. Phosphorescent ZnS. J.O.C. 1917, Vol. III, p 663. 1. Pure ZnS will give phosphorescence on heating, but not very much. 2. Impurities except of metals help towards luminescence. 3. Method of adding impurities not important. 4. Greater illuminating power was obtained where the ZnS was precipitated from a solution in which the zinc was in excess. An electric furnace was used. Below 650°C poor results were obtained. At 650°C to 900°C better results were obtained. Above 1110°C poor results were obtained. At first air was excluded and graphite crucibles were used. Later air was admitted, and porcelain crucibles used with good results. Four methods were used to excite the ZnS: light, X-rays, cathode rays, and Becquerel rays. When water or alcohol was used to wash the ZnS, the phosphorescence was greatly reduced.

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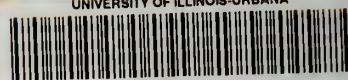
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